BOREAL ENVIRONMENT RESEARCH 21: 262–273
ISSN 1239-6095 (print) ISSN 1797-2469 (online)

Helsinki 23 May 2016

Production of highly oxidized organic compounds from ozonolysis of β-caryophyllene: laboratory and field measurements

Tuija Jokinen*, Oskari Kausiala, Olga Garmash, Otso Peräkylä, Heikki Junninen, Siegfried Schobesberger, Chao Yan, Mikko Sipilä and Matti P. Rissanen

*Department of Physics, Division of Atmospheric Sciences, P.O. Box 64, FI-00014 University of Helsinki, Finland (*corresponding author's e-mail: tuija.jokinen@helsinki.fi)*

Received 17 Dec. 2015, final version received 7 Mar. 2016, accepted 9 Mar. 2016

Jokinen T., Kausiala O., Garmash O., Peräkylä O., Junninen H., Schobesberger S., Yan C., Sipilä M. & Rissanen M.P. 2016: Production of highly oxidized organic compounds from ozonolysis of β-caryophyllene: laboratory and field measurements. *Boreal Env. Res.* 21: 262–273.

We conducted a laboratory investigation to identify highly-oxidized organic compounds formed in sesquiterpene ($C_{15}H_{24}$, SQT) ozonolysis. The dominant sesquiterpene previously identified from branch emissions of Scots pine, β-caryophyllene, was used for this study. Using the latest mass spectrometric methods, we identified several highly oxidized organic compounds corresponding to RO_2 radical, closed-shell monomer and dimer species. The most abundant compounds detected were monomers $C_{15}H_{24}O_{7,9,11}$ and $C_{15}H_{22}O_{9,11}$, and dimers $C_{29}H_{46}O_{12,14,16}$ and $C_{30}H_{46}O_{12,14,16}$. These oxidized organic compounds have very low saturation vapour pressures, an O-to-C ratio of about 0.3–0.9, and they are all classified as extremely low-volatility products (ELVOC). The molar yield of ELVOC was determined to be 1.7% ± 1.28%. Highly-oxidized organic compounds were also measured at a boreal forest site, and few possible β-caryophyllene oxidation products were identified, but the concentrations were extremely low, reaching a maximum of a few hundred thousand molecules cm^{-3} in spring.

Introduction

New nanoparticles formed from atmospheric vapours require very low-volatility compounds that are able to condense onto them and make them grow larger (Metzger *et al*. 2010, Riipinen *et al*. 2012). These compounds are very likely highly-oxidized reaction products of biogenic origin, such as processed monoterpene emissions from terrestrial vegetation. The recent discovery of extremely low-volatility organic compounds (ELVOC) from monoterpene ozonolysis suggests that these low-volatility products play a crucial role in the formation of secondary organic aerosol (SOA) (Ehn *et al*. 2014). In atmospheric conditions, the formation of these compounds could be explained by the gas-phase autoxidation process, which explains the formation of extremely low-volatility products via consecutive RO_2 radical isomerization and O_2 addition reactions (Crounse *et al*. 2013, Rissanen *et al*. 2014, Jokinen *et al*. 2014). The importance of ELVOC and other low-volatility products originating from monoterpenes and isoprene to cloud con-

Editor in charge of this article: Veli-Matti Kerminen

densation nuclei (CCN) production has recently been studied (Jokinen *et al*. 2015), indicating that these compounds may affect cloud formation properties and thereby the radiative balance of the planet. Detailed knowledge is required about other ELVOC production pathways and yields to explain the discrepancies between the modelled and measured SOAs (Heald *et al*. 2011).

To date the role of terpenes other than monoterpenes and isoprene in the formation of extremely low-volatile products has not been studied, but the formation of secondary organic aerosol from sesquiterpene ozonolysis has been reported with SOA yields from 6% up to almost 100%, depending on the relative humidity (Hoffmann *et al*. 1997, Winterhalter *et al*. 2009). Sesquiterpenes ($C_{15}H_{24}$, SQT) are highly reactive with NO_3 and OH radicals. Reactions of volatile organic compounds (VOC) with ozone (O_3) are generally slow, but in the atmosphere O_3 is the main oxidant removing SQT (Hoffamann *et al*. 1997). Studies have shown that the endocyclic double bond reacts with ozone more likely (> 95%) than the exocyclic double bond (Winterhalter *et al*. 2009). However, the information on reaction rates (k) of SQT with oxidants in the literature is limited, and some very contradictory k-values have been determined and published because of the difficulties with the high SQT reactivity (Bonn and Moortgat 2003). For example, k reported by Ghalaieny *et al*. (2012) is 320 times smaller than that given by Shu and Atkinson (1995). It has been suggested that pure SQTs are virtually impossible to detect in the ambient air because they immediately react with oxidants. In the USA, SQTs are estimated to account for about 9% of the non-methane hydrocarbon emissions (Helmig *et al*. 2006), and even values as high as 40% SQT's of the total BVOC emission rates have been recorded in northern Finland during spring (Tarvainen *et al*. 2004). If SQT had similar molar yields of ELVOC as monoterpenes (~1–7%), they might be as important to particle growth as monoterpene emissions are. In this study, we were focused on detecting the reaction products of SQT ozonolysis and determining their yields using both laboratory experiments and ambient air samples.

Here, we present the results of a laboratory study of β-caryophyllene (BCP) ozonolysis, where we measured the end products with the same mass spectrometric method that has been used previously for the direct ELVOC detection from the gas-phase (e.g. Ehn *et al*. 2014, Jokinen *et al*. 2014). We show that β-caryophyllene produces highly-oxidized reaction products in a similar autoxidation scheme to that of the monoterpenes. We report the yield of highly-oxidized species using the latest knowledge of the reaction rates, $k(\mathrm{SQT} + O_3)$ (Richters *et al*. 2015). We also report the first ambient measurements of selected highly-oxidized sesquiterpene species at the SMEAR II station in Hyytiälä, Finland, during spring, when terpene emissions are usually at their highest level.

Methods

Laboratory set-up and field site

All laboratory experiments were performed in a borosilicate flow reactor (approx. 205 cm long, inner diameter of 4.7 cm) with a residence time (τ) of about 18 s. All measurements were conducted at the room temperature (~293–296 K) and at the ambient pressure. Liquid β-caryophyllene (≥ 98%) was purchased from Sigma-Aldrich. The gas sample was made by bubbling nitrogen gas through the liquid BCP precursor which was then directed to the flow tube using variable flow rates of the carrier gas. Ozone was produced with an ozone generator (Dasibi 1008-PC) and the ozone concentration was monitored with a Thermo Fisher 49-ozone analyser. Ozone concentration was kept constant throughout the experiments (at about 20 ppbv after dilution in the flow tube). Mixing of the sample gas with the oxidant was done in the front of the flow tube. BCP concentrations varying between 17–335 ppbv were used in these experiments (concentration after dilution in the flow tube). An OH scavenger was not used during these experiments.

To calculate the concentration of BCP in the sample flow, we used a saturation vapour pressure of 4.16 Pa which was obtained using the EPI programme suite (United States Environmental Protection Agency 2015). Dilution in the flow tube was taken into account using the sample flow

of the mass spectrometer, 10–12 l min^{-1}, which was also the total flow of the flow reactor. The reaction rate coefficient [k(BCP + O_3) = 1.1×10^{14} cm^3 molecules^{-1} s^{-1}] was taken from the literature (Shu and Atkinson 1995, Richters *et al*. 2015). The reacted BCP concentration was calculated according to: [reacted BCP] = $k \times [O_3] \times$ [BCP] $\times$ τ (τ = 18 s).

Ambient measurements were made during the HydeSpring 2011 campaign at the SMEAR II station in Hyytiälä (Hari and Kulmala 2005), southern Finland, during which both ambient ion and neutral compounds were detected simultaneously using the latest mass spectrometric methods (*see* section 'Instrumentation' below). The campaign lasted from early March to the second week of April. The last two weeks of the data from the campaign were used for this study. This was because the emission rates of sesquiterpenes have been reported to be at their highest level during early spring, when temperatures rise with increasing radiation and trees start emitting more VOCs (Tarvainen *et al*. 2004, Aalto *et al*. 2015).

Instrumentation

The chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (CI-APi-TOF) was used to detect the formed sesquiterpene ozonolysis products in the experiments. The CI-APi-TOF was run in the negative ion mode and concentrated nitric acid (HNO_3) was ionized to reagent ions, nitrate and its oligomers (NO_3^-, $HNO_3NO_3^-$ and $(HNO_3)_2NO_3^-$) with a soft X-ray ionizer (Hamamatsu L9490) in the laboratory experiments. The chemical ionization inlet is a design adopted from Eisele and Tanner (1993) and modified to be used without the radioactive source and to fit the APi-TOF. In the field measurements, an Am-241 α-radiation was used for ionization (for details *see* Jokinen *et al*. 2012). Using different ionization methods in the field and laboratory experiments for creating the reagent ions did not affect the end product detection. The only difference between the methods was the higher absolute count rate due to more efficient ion production in the Americium source.

After ionization, the nitrate ions are guided to surround the sample air that travels in the centre of the inlet gas-stream with a flow rate of 10 l min^{-1}, without any wall contact. Reagent ions in the sheath air are guided to meet the sample flow using electric fields. The sample is ionized either via a proton transfer, e.g. HA + NO_3^- → A^- + HNO_3, or via clustering with the reagent ion, e.g. HA + NO_3^- → HA • NO_3^-. In this study, the highly-oxidized sesquiterpene products were all detected as nitrate clusters. Concentrations of the highly-oxidized organics, [$ELVOC_{SQT}$], in the laboratory experiments were calculated using signal normalization with the sum of reagent ions [NO_3^-, $HNO_3NO_3^-$ and $(HNO_3)_2NO_3^-$] and the calibration factor for sulphuric acid, $C = 5 \times 10^9$ molecules cm^{-3} (Jokinen *et al*. 2012):

$$[ELVOC_{SQT}] = \Sigma SQTpa/\Sigma Rpa \times C, \quad (1)$$

where SQTpa are the SQT peak areas, and Rpa are the reagent peak areas (NO_3^- + $HNO_3NO_3^-$ + $(HNO_3)_2NO_3^-$).

Ambient concentrations were calculated using $C = 1.89 \times 10^{10}$ molecules cm^{-3}, which includes the losses to the inlet tubing (length 60 cm).

The uncertainty related to ELVOC measurements is based on the work of Ehn *et al*. (2014) who demonstrated that the collision frequency of an ELVOC with the charger ion is almost to equal to that of SA and the charger ions. Thus, we assumed the collision-limited charging of ELVOC in our experiments to have an uncertainty of ±50%. Other sources of uncertainty include the mass flow controller flow errors (according to the manufacturer ±1%), ozone monitor error (according to the manufacturer ±1%), flow controller errors (according to the manufacturer ±2%), uncertainty in the BCP vapour pressure of ±50% (Helmig *et al*. 2003, United States Environmental Protection Agency 2015), error due to the residence time in the flow tube (error in the flow rate and volume of the flow tube) of ±3% and uncertainty in the reaction rate coefficient of ±10% (Shu and Atkinson 1995). By including a simple first-order diffusion limited wall loss correction, the obtained yields would be roughly 30% higher (i.e. with a diffusion coefficient the diffusion-limited wall loss, $k = 3.65D/r^2 = 0.033$ s^{-1}, obtained using D = 0.05 cm^2 s^{-1} and r = 2.35 cm; Ehn *et al*. 2014). The total uncertainty was calculated using the

propagation of uncertainties. The total uncertainty of the concentrations reported was estimated to be ±75% when including all the above errors. During the HydeSpring2011 campaign, the CI-APi-TOF was used without an ion filter, so the reported concentrations included a small fraction of naturally-charged ions (usually < 5%) that contributed to the total signal.

During the field campaign, the naturally-charged ion composition was also measured during the spring months, using an APi-TOF without any ionization prior to the mass spectrometer. We used a wide (40 mm inner diameter) steel sample tube to suck in ambient air at a large flow rate to reduce wall losses. Out of the total flow, 6 l min^{-1} were drawn toward the APi-TOF orifice via a 30-cm-long tube (8 mm inner diameter) located inside of and at the centre of the larger tube. The orifice itself drew a flow of 0.8 l min^{-1} into the instrument. The larger total flow sampled through the wider tube was adjusted to optimize transmission of ions from the ambient air into the orifice. The APi-TOF was run in the negative ion mode, so that we were able to compare the composition of charged and neutral species during the campaign.

Theory behind BCP ozonolysis

In the atmosphere, ozonolysis is estimated to remove > 98% of the BCP (Hoffmann *et al*. 1997). In the case of BCP, ozone will attack the endocyclic double bond about 100 times faster than the exocyclic double bond (Nguyen *et al*. 2009), forming a primary ozonide (POZ, *see* scheme for ozonolysis in Fig. 1). Reaction with the exocyclic double bond also leads to POZ formation, but since its significance has been found negligible, we only considered the reaction of ozone and endocyclic double bond in detail. Two possible conformers, POZ_1 and POZ_2, exist from the initial reaction with ozone and their isomerization into each other is relatively easy because of the small energy barrier separating the two structures. Chemically active POZs can be stabilized in collisions with the carrier gas, or they can break the ring structure leading to the formation of two different Criegee intermediates (CI), CI_1 and CI_2 (Fig. 1).

In the atmosphere, the ring structure of a stabilized primary ozonide is broken within seconds, leading to the formation of a thermalized CI. These do not usually react in unimolecular but in bimolecular reactions with e.g. SO_2, water and organic acids. A fast decomposition of the POZ leads to the formation of an excited CI, the behaviour of which we now examine closer. The formed CIs also have possible *anti-* and *syn-*conformers, but they do not isomerize as easily as the initial POZs. In this case the *syn-*confomer structure is meant when the oxygen in the radical centre points towards the alkylic group of the compound (also in Fig. 1).

In the case of excited CIs, two fast unimolecular reactions are possible before the stabilization with the surrounding carrier gas occurs. One of them is the formation of a dioxirane-type intermediate product and the other one is a 1,4-hydrogen shift creating a vinylic hydroperoxy radical. The latter channel is possible for CI_{1A}, CI_{1B} and CI_{2A} intermediates of Scheme 1 (Nguyen *et al*. 2009). After a loss of OH radical from the hydroperoxy radical, the molecule is left with an alkyl radical centre that can accommodate an oxygen molecule, forming a RO_2 radical. After the formation of RO_2, an intramolecular hydrogen shift can take place, starting autoxidation of the molecule (Crounce *et al*. 2013). This is a viable reaction path to extremely low-volatile organic compounds (ELVOC). Nguyen *et al*. (2009) calculated the relative distribution of intermediate products (RAD1 and RAD2) for the ozonolysis of the endocyclic double bond of BCP. The results for RAD1A, RAD1B and RAD2A in ozonolysis scheme (Fig. 1) were 0.1%, 6.7% and 1.4%, respectively, and thus the maximum yield of the formed alkyl radicals is estimated to be 8.2% and corresponds to the maximum theoretical yield of ELVOC obtained from the ozonolysis. However, the radicals can be lost in multiple different reaction pathways that do not form ELVOC (e.g. Rissanen *et al*. 2014), which can result in much lower yields for ELVOC.

Estimating vapour pressures of the BCP oxidation products

We estimated the volatility of the highly-oxi-

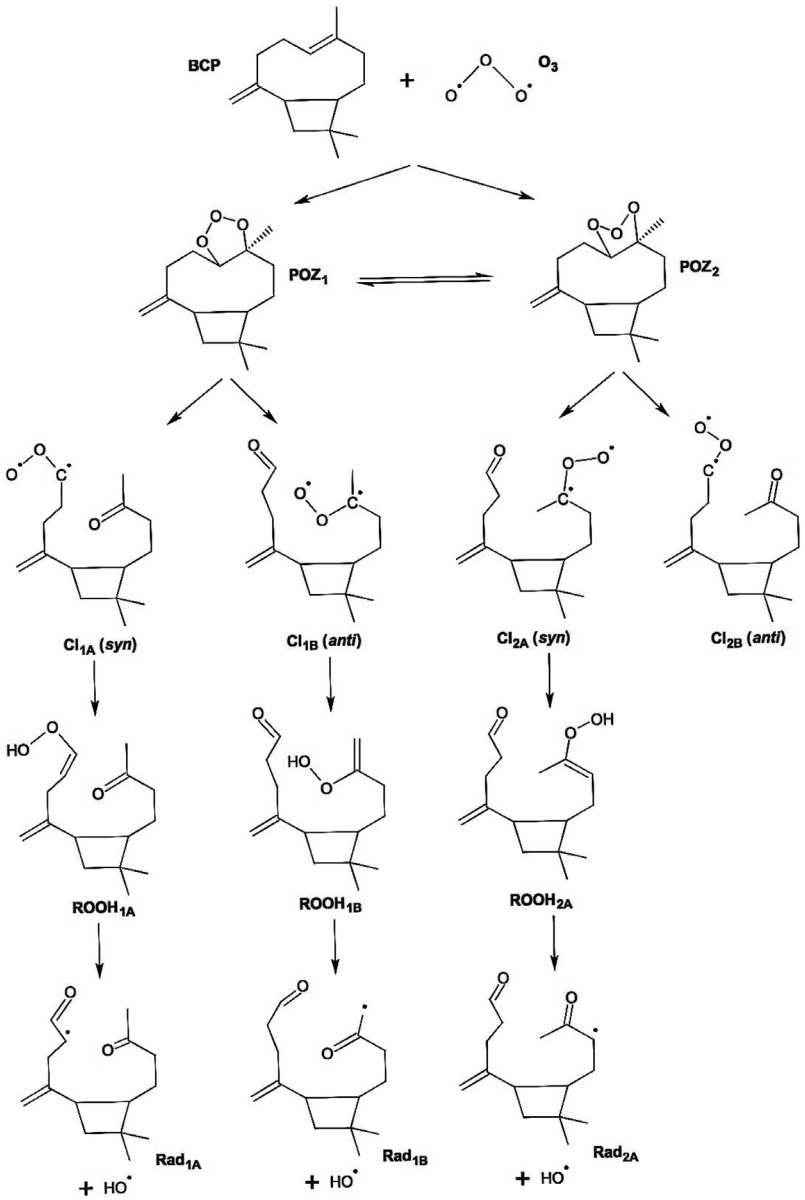

Fig. 1. Scheme of ozonolysis of β-caryophyllene: in the beginning, ozone attacks the endocyclic double bond forming a primary ozonide (POZ), from which the reaction can proceed through four different Criegee intermediates ($Cl_{1\,A,B}$ and $Cl_{2\,A,B}$).

dized compounds according to their carbon oxidation state oSc (Droll *et al*. 2011),

$$\mathrm{oSC} = 2\frac{n_O}{n_C} - \frac{n_H}{n_C}, \quad (2)$$

where n_C is the number of carbon atoms, n_H is the number of hydrogen atoms and n_O is the number of oxygen atoms in the molecule; the O-to-C ratio; and saturation concentration, C^0 (Donahue *et al*. 2011)

$$\log_{10}C^0 = \left(n_C^0 - n_C\right)b_C - n_O b_O - 2\frac{n_C n_O}{n_C + n_O}b_{CO}, \quad (3)$$

where b_C is the carbon–carbon interaction term (about 0.475), b_O is the oxygen-oxygen interaction term (about 2.3), b_{CO} is the carbon-oxygen nonideality (about –0.3) and $n_O{}^0$ is the carbon number at $C^0 = 1\ \mu g\ m^{-3}$ for alkane. These terms were adopted from Donahue *et al*. (2011).

After calculating these three parameters we found that all the detected SQT oxidation prod-

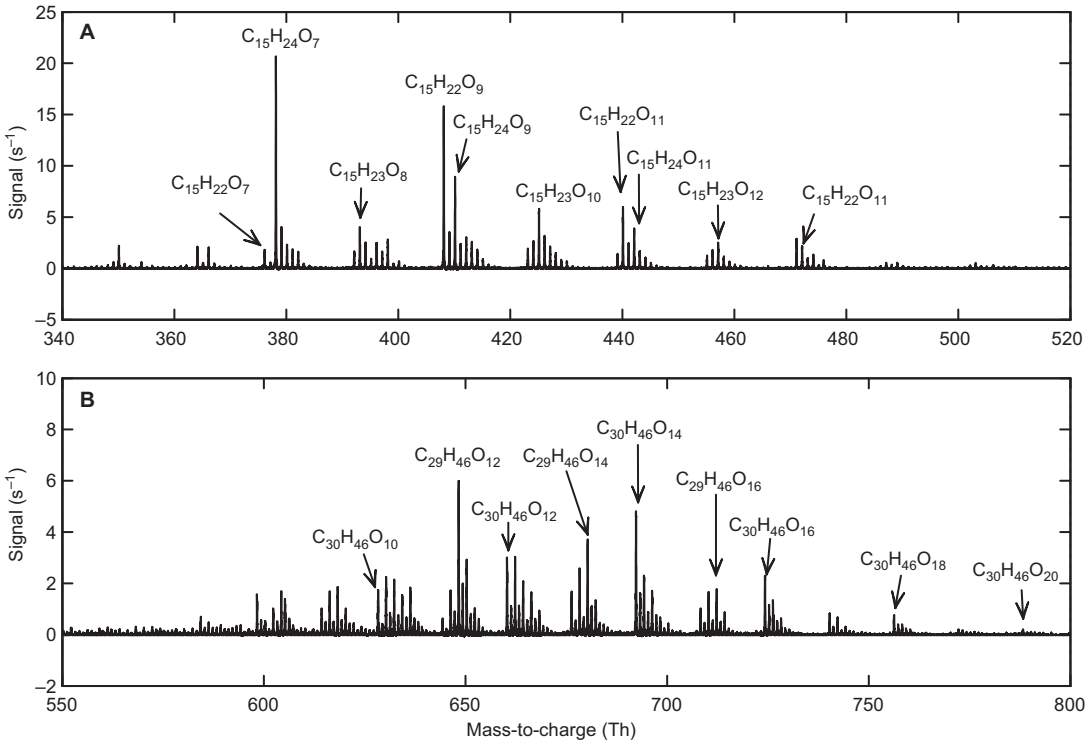

Fig. 2. The CI-APi-TOF spectra detected during β-caryophyllene oxidation by ozone in a flow tube. (**A**) the most abundant highly-oxidized organic monomers with a C_{15} carbon skeleton, and the molecular structure of β-caryophyllene. (**B**) the detected dimers with a C_{29}–C_{30} carbon skeleton. All products were detected as NO_3^- clusters.

ucts can be classified as extremely low-volatile organic compounds if they have an oxygen number of five or more ($C_{15}H_{22}O_5$ upwards), meaning that these compounds have a saturation concentration of $\log_{10}C^0/\mu g^{-1}\ m^{-3} < -3.5$ (Donahue *et al*. 2011).

Results and discussion

Laboratory experiments

We started the laboratory experiments with β-caryophyllene injection into the flow tube, followed by addition of ozone, to see whether the reaction product spectrum would reveal similar highly oxidized compounds to those measured with several different monoterpenes (Ehn *et al*. 2014, Jokinen *et al*. 2015). In the mass spectrum, the formed monomers with a C_{15} carbon skeleton and dimers with a C_{29}–C_{30} carbon skeleton with high oxygen content were detected in the mass-to-charge ratio (*m*/*z*) ranges 340–520 Th and 350–800 Th, respectively (Fig. 2).

The most intense signals were observed in the monomer range at *m*/*z* of 378.14 Th and 408.11 Th corresponding to $C_{15}H_{24}O_7$ and $C_{15}H_{22}O_9$, respectively. The highly-oxidized ELVOC RO_2 radicals produced in the ozonolysis initiated autoxidation, as suggested by Jokinen *et al*. (2014), were detected and identified as $C_{15}H_{23}O_{8,10,12}$ (with 2–4 possible –OOH groups). The corresponding closed-shell monomers were also detected and they had a composition of $C_{15}H_{22}O_{7,9,11,13}$ (loss of –OH from the corresponding RO_2). We found several peaks that could be explained by the autoxidation from ozonolysis, and also by OH-initiated reactions, in the monomer range (Table 1). However, the peaks with an elemental composition of $C_{15}H_{24}O_{7,9,11}$ cannot be explained by pseudo-unimolecular autoxidation steps only. Since the flow tube experiments were done in a relatively high concentration of BCP, the fate of the formed RO_2 radicals will also be

the reaction with other RO_2 radicals. This way an ELVOC RO_2 radical (e.g. $C_{15}H_{23}O_8\cdot$) could undergo a reaction with RO_2 radical to form a RO radical ($C_{15}H_{23}O_7\cdot$). After an intramolecular H-transfer (formation of the next RO_2 radical) and a further reaction with HO_2 can explained the peak identified as $C_{15}H_{24}O_7$. Further autoxidation steps before the RO_2 + RO_2 reaction will lead to the production of the detected $C_{15}H_{24}O_9$ and $C_{15}H_{24}O_{11}$. The strongest dimer signals were identified as $C_{29}H_{46}O_{12,14,16}$ and $C_{30}H_{46}O_{12,14,16}$ (Fig. 2).

From these experiments, we can conclude that β-caryophyllene, and thus probably also other endocyclic SQTs, are able to produce highly-oxidized reaction products under atmospheric conditions. The detected compounds, from $C_{15}H_{23}O_5$ to $C_{15}H_{23}O_{13}$, have an O-to-C ratio from 0.33 to 0.87, carbon oxidation state (oSC) from –0.8 to 0.27 and $\log_{10}C^0/\mu g^{-1}\ m^{-3}$ from –4.5 to –21.0.

We calculated the total yield for highly-oxidized organic compounds from β-caryophyllene ozonolysis (without OH-scavenger) using a reaction rate of 1.1×10^{-14} cm^3 molecules^{-1} s^{-1} [k(BCP + O_3)] that is obtained from both theoretical calculations (Nguyen *et al*. 2009) and experimental works (Shu and Atkinson 1995, Winterhalter *et al*. 2009, Richters *et al*. 2015). However, it should be noted that the values reported in the literature for the same reaction rate vary up to three orders of magnitude, depending on the method used (Ghalaieny *et al*. 2012). Ozonolysis of BCP produces OH radicals (~6%–10% from endocyclic and 16.4% from exocyclic double bond reactions; Winterhalter *et al*. 2009, Shu and Atkinson 1995), and since no OH-scavenger was used in this experiment, the oxidation of BCP with OH is competing with ozonolysis. We calculated the total yield of highly-oxidized organic compounds (ELVOC) to be 1.7% ± 1.28%. This result was obtained when only the data points closest to the linear fit (magenda squares in Fig. 3) and the reaction rate (k) from Richters *et al*. (2015) were used. When the entire data range was included, the ELVOC yield dropped to 1.1% ± 0.83%, which is still within the measurement uncertainty.

Field measurements

The field measurement campaign was carried out during the spring months in 2011 at the SMEAR II station. In Finland, spring is the season when emission rates of terpenes from the forest are increasing rapidly with the increasing temperature, sometimes even creating bursts of emissions (Tarvainen *et al*. 2004, Aalto *et al*. 2015). We followed the most abundant compositions observed in the β-caryophyllene ozonolysis system during the last two weeks of the campaign (between 28 March and 12 April 2011), as before this period no signals of SQT oxidation products were observed. Since the spectra in ambient air are more diverse than the ones in laboratory conditions and concentrations are generally lower, we used the knowledge from the laboratory experiments with the exact mass, mass defect and isotopic patterns of each compound to identify them from other possible elemental compositions. The peak intensities of the possible BCP products detected in the mass spectrum in Hyytiälä were very low (Fig. 4). There were many other possibilities for the same integer mass-to-charge ratios, but we were able to fit the peaks according to the exact mass of a few highly-oxidized BCP products, and thus quantify concentrations of these species. However, it has to be noted that oxidation of other SQTs than BCP will likely lead to products with

Table 1. Calculated elemental compositions and mass-to-charge ratios (including the charger ion, NO_3^-) of some of the oxidation products explained by autoxidation steps in the monomer range. Both ozone and OH-initiated reaction products are presented. Mass-to-charge ratios set in boldface were detected in our laboratory experiments.

m/z	RO_2 (O_3)	*m/z*	Monomer (O_3)
361	$C_{15}H_{23}O_6$	**344**	$C_{15}H_{22}O_5$
393	$C_{15}H_{23}O_8$	**376**	$C_{15}H_{22}O_7$
425	$C_{15}H_{23}O_{10}$	**408**	$C_{15}H_{22}O_9$
457	$C_{15}H_{23}O_{12}$	**440**	$C_{15}H_{22}O_{11}$
489	$C_{15}H_{23}O_{14}$	**472**	$C_{15}H_{22}O_{13}$
521	$C_{15}H_{23}O_{16}$	504	$C_{15}H_{22}O_{15}$
	RO_2 (OH)		Monomer (OH)
347	$C_{15}H_{25}O_5$	**330**	$C_{15}H_{24}O_4$
379	$C_{15}H_{25}O_7$	**362**	$C_{15}H_{24}O_6$
411	$C_{15}H_{25}O_9$	**394**	$C_{15}H_{24}O_8$
443	$C_{15}H_{25}O_{11}$	**426**	$C_{15}H_{24}O_{10}$
475	$C_{15}H_{25}O_{13}$	**458**	$C_{15}H_{24}O_{12}$

similar elemental compositions, and thus these identified peaks could have additional contribution from other SQTs. Ambient measurement results were thus presented as they were oxidation products of any ambient SQT.

Observation of electrically neutral SQT oxidation products

Concentrations of the three detected, highly-oxidized organic neutral molecules from SQT oxidation followed each other during our measurements (Fig. 5A). Their diurnal patterns were quite similar to the corresponding naturally-charged ions (Fig. 6), with the exception of the neutral BCP oxidation products which reached their maximum concentrations during midday. Both neutral molecules and ions had another peak in the late evening. The higher neutral SQT oxidation product concentrations during

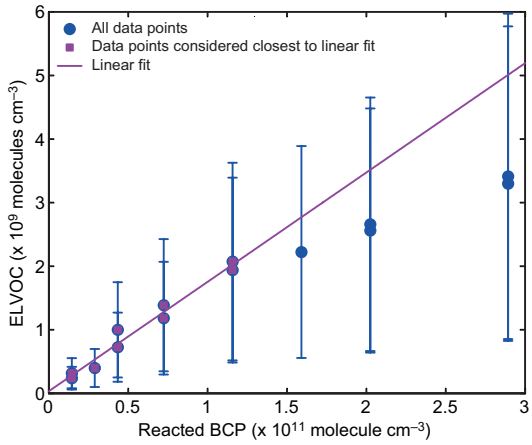

Fig. 3. Reacted β-caryophyllene ($k \times [BCP] \times [O_3] \times \tau$; τ = 18 s) as a function of the detected total ELVOC concentration measured with the CI-APi-TOF. The error bars are ±75% uncertainty.

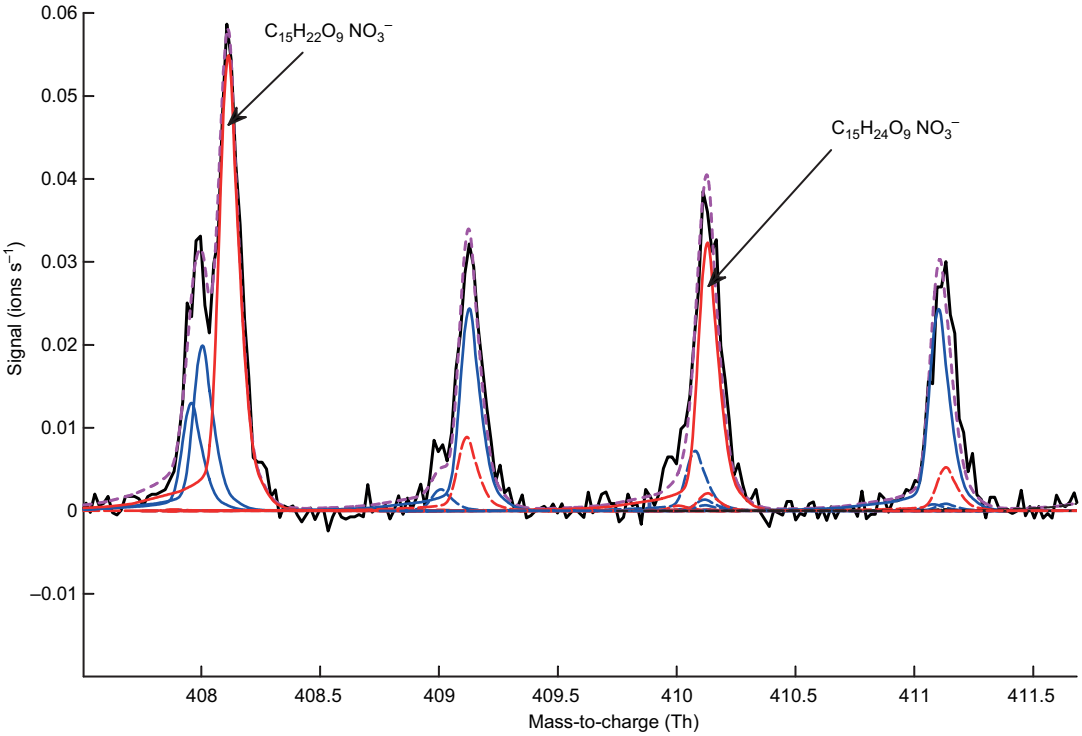

Fig. 4. Mass spectrum measured in the spring at the SMEAR II station with the CI-APi-TOF. The peaks colored in red depict the peak fitting according to the exact mass of the selected compound. The blue peaks represent other fitted, mostly unidentified peaks. Isotopes are depicted with dashed lines. Magenta dashed line represents the sum of the fitted peaks.

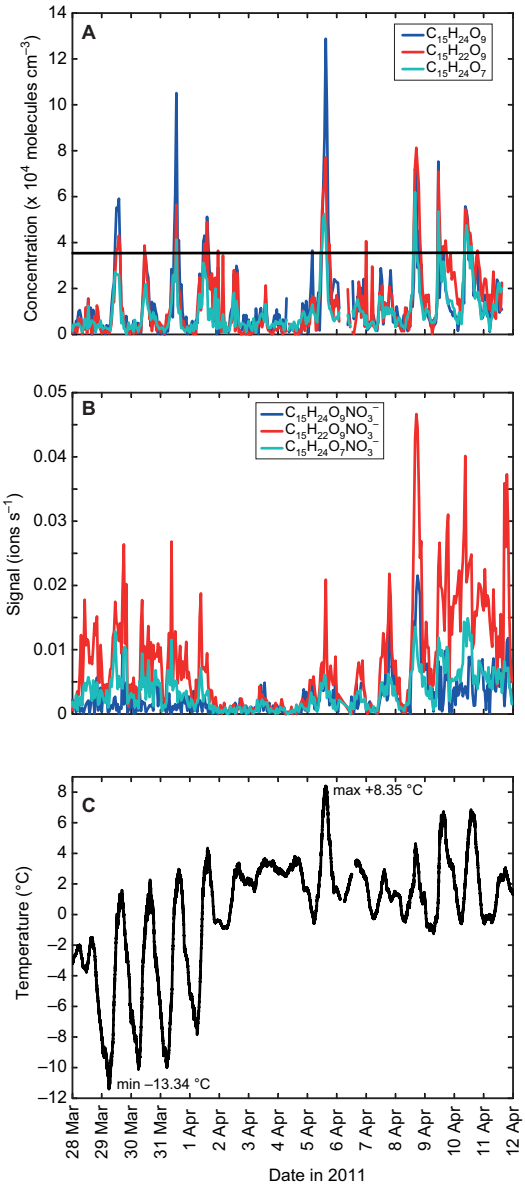

Fig. 5. Time series of highly-oxidized organics detected in March–April 2011 during the HydeSpring2011 campaign. (**A**) CI-APi-TOF measurements of neutral compounds, (**B**) APi-TOF measurements of naturally-charged ions, and (**C**) air temperatures measured 4.2 m above ground level. The neutral and the ion data are 60-min averages, and peaks were separated using a high-resolution peak fitting according to the exact mass of each compound. Three possible β-caryophyllene products were identified: $C_{15}H_{24}O_9$, $C_{15}H_{22}O_9$ and $C_{15}H_{24}O_7$ (detected as NO_3^- clusters). The black thick line in **A** represents the limit of detection (LOD) for sulphuric acid that was used for calibration (Jokinen *et al.* 2012). Uncertainty in highly-oxidized organic concentration is estimated to be ±75%.

daytime were possibly due to the emission rate of SQT from vegetation being the highest during that period, when temperatures are much higher than at nighttime. The nighttime increase in SQT signals was possibly due to the change in the oxidation chemistry, the ozonolysis being the prominent oxidation channel after sunset. The maximum concentrations of highly-oxidized BCP ozonolysis products were just above the detection limit (LOD) for sulphuric acid (3.6×10^4 molecules cm^{-3}) (Jokinen *et al.* 2012), reaching a maximum of a few 10^5 molecules cm^{-3}. The LOD was in this case used as a guideline for the extremely low-volatile molecules assuming they would have similar volatilities as sulphuric acid. The highest concentration during the field measurements was observed from $C_{15}H_{24}O_9$.

Observations of SQT oxidation products in naturally-charged ions

During the first week (Fig. 5B), the signals of all of the detected highly-oxidized naturally-charged ions were weak and their identification was difficult to some extent due to several different compounds present within the same mass spectral peaks. Those days had high concentrations of bisulphate (sulphuric acid) and its oligomer ions, the signals of which contributed to the measured ion distribution. As a strong acid with very low proton affinity, sulphuric acid was the dominant ion and thus only a few other signals were detected during daytime. During the last week of the measurements, we saw an indication of the effect of the rising temperature on the BCP ozonolysis product signals (Fig. 5C). The most intense signal observed was from $C_{15}H_{22}O_9NO_3^-$, with an O-to-C ratio of 0.6. The maximum signals of the BCP ozonolysis products were seen around midday or late in the evening when sulphuric acid signals decreased. Altogether, even when the SQT oxidation products were at their highest level (in the evening), their maximum contribution to the total ion counts detected was ~0.02%, however a slight positive trend of signals increasing towards the end of spring was present. A longer period should be recorded for more detailed analysis of BCP oxidation product evolution in the ambient air.

Conclusions

This study reports important information on the ozonolysis reaction products of one of the most emitted sesquiterpene, β-caryophyllene. This extremely reactive compound with atmospheric ozone was shown to produce low-volatile organic compounds that were detected in laboratory and ambient-air measurements. The spectrum obtained from β-caryophyllene ozonolysis showed similar patterns as that of ELVOC [part deleted] (Ehn *et al*. 2014, Jokinen *et al*. 2015, Schobesberger *et al*. 2013). Formations of oxidized monomers with a C_{15} carbon skeleton and dimers with a C_{30} carbon skeleton were detected immediately when ozone was introduced into the BCP system. In the laboratory experiments, we positively identified several highly-oxidized organic compounds in the mass spectra corresponding to the RO_2 radical, monomer and dimer species. The most abundant monomer species in this study were $C_{15}H_{24}O_{7\text{-}9\text{-}11}$ and $C_{15}H_{22}O_{9\text{-}11}$, and the most intense dimer signals were identified as $C_{29}H_{46}O_{12,14,16}$ and $C_{30}H_{46}O_{12,14,16}$. These oxidized organic compounds have the O-to-C ratio of ~0.3–0.9 in the monomer and ~0.3–0.6 in the dimer range. The volatility of these reaction products was evaluated using several quantities, including their O-to-C ratio, and all of the detected compounds were classified as extremely low-volatile organic compounds due to their saturation concentration ($\log_{10}C^0/\mu g^{-1}$ m^{-3} < 3.5; Donahue *et al*. 2011).

The yield of ELVOC from BCP ozonolysis without using an OH scavenger was determined to be 1.7% ± 1.28%, which seems reasonable as the maximum theoretical yield is ~8%. The lower yield may be explained by other reactions occurring before the autoxidation sequence takes place, determining the fate of the initially-formed primary ozonide. If the breaking of the POZ needed for radical formation is hindered, it can lead to a dramatic transformation in the dominant oxidation pathway from a radical-forming process at a low carbon number (isoprene and maybe monoterpenes) to a secondary ozonide-forming process at a high carbon number like in the case of sesquiterpenes (Chuong *et al*. 2004), thereby also decreasing the possible low-volatile product formation.

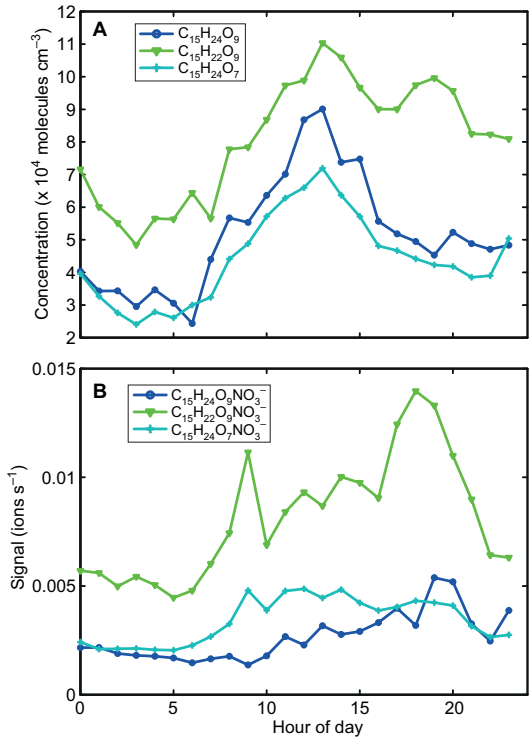

Fig. 6. Diurnal patterns of detected (**A**) neutral and (**B**) naturally-charged ions β-caryophyllene oxidation products averaged over a period of 15 days. The data were collected in Hyytiälä, southern Finland, between 28 March and 12 April 2011.

Highly-oxidized organic compounds were also measured at the the SMEAR II station. Three sesquiterpene oxidation products, originating from BCP or other SQTs, were identified in both naturally-charged ions and in neutral form in the ambient air in the spring of 2011. The observed concentrations of the neutral species were extremely small, reaching a maximum of a few hundred thousand molecules cm^{-3} during the two weeks of measurements. In naturally-charged ions, the SQT ELVOC contributed a minimal signal that was up to 0.02% of the total ion signal detected at this site.

The contribution of low-volatile products from the SQT ozonolysis (BCP and others) may affect the SOA burden and contribute to aerosol growth in places where high emission rates of SQT are observed, e.g. in the USA or northern Finland (Tarvainen *et al*. 2004). BCP ozonoly-

sis products are classified as ELVOC when the number of oxygen atoms in the product molecule reaches five or more, after which they are able to affect nanoparticle growth by condensing onto them. However, the impact might be important only locally or regionally if the emissions are high compared with emissions other important VOCs such as monoterpenes and certain anthropogenic hydrocarbons. Further and more exact information is needed on the reactivity of different SQTs emitted by terrestrial vegetation before we can evaluate the effect of SQT ELVOC on atmospheric new particle formation and growth.

Acknowledgements: We thank the tofTools team for providing tools for mass spectrometry analysis. We acknowledge the Academy of Finland Centre of Excellence (grant no. 272041), the European Research Council Advanced Grant (ATM-NUCLE, grant no. 227463) and ERC Starting Grant (COALA), and innovation programme (ACTRIS-2, grant no. 654109) for funding.

References

Aalto J., Porcar-Castell A., Atherton J., Kolari P., Pohja T., Hari P., Nikinmaa E., Petäjä T. & Bäck J. 2015. Onset of photosynthesis in spring speeds up monoterpene synthesis and leads to emission bursts. *Plant Cell Environ*. 38: 2299–2312.

Bonn B. & Moortgat G.K. 2003. Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons. *Geophys. Res. Lett*. 30: 2–5.

Chuong B., Zhang J. & Donahue N.M. 2004. Cycloalkene ozonolysis: collisionally mediated mechanistic branching. *J. Am. Chem. Soc*. 126: 12363–12373.

Crounse J.D., Nielsen L.B., Jørgensen S., Kjaergaard H.G. & Wennberg P.O. 2013. Autoxidation of Organic Compounds in the Atmosphere. *J. Phys. Chem. Lett*. 4: 3513–3520.

Donahue N.M., Epstein S.A., Pandis S.N. & Robinson A.L. 2011. A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics. *Atmos. Chem. Phys*. 11: 3303–3318.

Donahue N.M., Kroll J.H., Pandis S.N. & Robinson A.L. 2012. A two-dimensional volatility basis set — Part 2: Diagnostics of organic-aerosol evolution. *Atmos. Chem. Phys*. 12: 615–634.

Ehn M., Thornton J.A., Kleist E., Sipilä M., Junninen H., Pullinen I., Springer M., Rubach F., Tillmann R., Lee B., Lopez-Hilfiker F., Andres S., Acir I.-H., Rissanen M., Jokinen T., Schobesberger S., Kangasluoma J., Kontkanen J., Nieminen T., Kurtén T., Nielsen L.B., Jørgensen S., Kjaergaard H.G., Canagaratna M., Maso M.D., Berndt T., Petäjä T., Wahner A., Kerminen V.-M., Kulmala M., Worsnop D.R., Wildt J. & Mentel T.F. 2014. A large source of low-volatility secondary organic aerosol. *Nature* 506: 476–479.

Eisele F.L. & Tanner D.J. 1993. Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere. *J. Geophys. Res*. 98: 9001–9010.

Ghalaieny M., Bacak A., McGillen M., Martin D., Knights A.V., O'Doherty S., Shallcross D.E. & Percival C.J. 2012. Determination of gas-phase ozonolysis rate coefficients of a number of sesquiterpenes at elevated temperatures using the relative rate method. *Phys. Chem. Chem. Phys*. 14: 6596–6602.

Hari P. & Kulmala M. 2005. Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II). *Boreal Env. Res*. 10: 315–322.

Heald C.L., Coe H., Jimenez J.L., Weber R.J., Bahreini R., Middlebrook A.M., Russell L.M., Jolleys M., Fu T.-M., Allan J.D., Bower K.N., Capes G., Crosier J., Morgan W.T., Robinson N.H., Williams P.I., Cubison M.J., DeCarlo P.F. & Dunlea E.J. 2011. Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model. *Atmos. Chem. Phys*. 11: 12673–12696.

Helmig D., Ortega J., Guenther A., Herrick J.D. & Geron C. 2006. Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US. *Atmos. Environ*. 40: 4150–4157.

Helmig D., Revermann T., Pollmann J., Kaltschmidt O., Jiménez Hernández A., Bocquet F. & David D. 2003. Calibration system and analytical considerations for quantitative sesquiterpene measurements in air. *J. Chromatography A* 1002: 193–211.

Hoffmann T., Odum J.R., Bowman F., Collins D., Klockow D., Flagan R.C. & Seinfeld J.H. 1997. Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *J. Atmos. Chem*. 26: 189–222.

Jokinen T., Sipilä M., Junninen H., Ehn M., Lönn G., Hakala J., Petäjä T., Mauldin R.L., Kulmala M. & Worsnop D.R. 2012. Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF. *Atmos. Chem. Phys*. 12: 4117–4125.

Jokinen T., Sipilä M., Richters S., Kerminen V.-M., Paasonen P., Stratmann F., Worsnop D., Kulmala M., Ehn M., Herrmann H. & Berndt T. 2014. Rapid autoxidation forms highly oxidized RO_2 radicals in the atmosphere. *Angew. Chem. Int. Ed. Engl*. 53: 14596–14600.

Jokinen T., Berndt T., Makkonen R., Kerminen V.-M., Junninen H., Paasonen P., Stratmann F., Herrmann H., Guenther A.B., Worsnop D.R., Kulmala M., Ehn M. & Sipilä M. 2015. Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications. *Proc. Natl. Acad. Sci. USA* 112: 7123–7128.

Kroll J.H., Donahue N.M., Jimenez J.L., Kessler S.H., Canagaratna M.R., Wilson K.R., Altieri K.E., Mazzoleni L.R., Wozniak A.S., Bluhm H., Mysak E.R., Smith J.D., Kolb C.E. & Worsnop D.R. 2011. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nature Chem*. 3: 133–139.

Metzger A., Verheggen B., Dommen J., Duplissy J., Prevot

A.S.H., Weingartner E., Riipinen I., Kulmala M., Spracklen D. V, Carslaw K.S. & Baltensperger U. 2010. Evidence for the role of organics in aerosol particle formation under atmospheric conditions. *Proc. Natl. Acad. Sci. USA* 107: 6646–6651.

Nguyen T.L., Winterhalter R., Moortgat G., Kanawati B., Peeters J. & Vereecken L. 2009. The gas-phase ozonolysis of beta-caryophyllene (C(15)H(24)). Part II: A theoretical study. *Phys. Chem. Chem. Phys.* 11: 4173–4183.

Richters S., Herrmann H. & Berndt T. 2015. Gas-phase rate coefficients of the reaction of ozone with four sesquiterpenes at 295 ± 2 K. *Physical Chem. Chem. Phys.* 17: 11658–11669.

Riipinen I., Yli-Juuti T., Pierce J.R., Petäjä T., Worsnop D.R., Kulmala M. & Donahue N.M. 2012. The contribution of organics to atmospheric nanoparticle growth. *Nature Geosci.* 5: 453–458.

Rissanen M.P., Kurtén T., Sipilä M., Thornton J. a, Kangasluoma J., Sarnela N., Junninen H., Jørgensen S., Schallhart S., Kajos M.K., Taipale R., Springer M., Mentel T.F., Ruuskanen T., Petäjä T., Worsnop D.R., Kjaergaard H.G. & Ehn M. 2014. The formation of highly oxidized multifunctional products in the ozonolysis of cyclohexene. *J. Am. Chem. Soc.* 136: 15596–15606.

Schobesberger S., Junninen H., Bianchi F., Lonn G., Ehn M., Lehtipalo K., Dommen J., Ehrhart S., Ortega I.K., Franchin A., Nieminen T., Riccobono F., Hutterli M., Duplissy J., Almeida J., Amorim A., Breitenlechner M., Downard A.J., Dunne E.M., Flagan R.C., Kajos M., Keskinen H., Kirkby J., Kupc A., Kurten A., Kurten T., Laaksonen A., Mathot S., Onnela A., Praplan A.P., Rondo L., Santos F.D., Schallhart S., Schnitzhofer R., Sipila M., Tome A., Tsagkogeorgas G., Vehkamaki H., Wimmer D., Baltensperger U., Carslaw K.S., Curtius J., Hansel A., Petaja T., Kulmala M., Donahue N.M. & Worsnop D.R. 2013. Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules. *Proc. Natl. Acad. Sci. USA* 110: 17223–17228.

Shu Y. & Atkinson R. 1995. Atmospheric lifetimes and fates of a series of sesquiterpenes. *J. Geophys. Res.* 100: 7275–7281.

Tarvainen V., Hakola H., Hellén H., Bäck J., Hari P. & Kulmala M. 2004. Temperature and light dependence of the VOC emissions of Scots pine. *Atmos. Chem. Phys. Discuss.* 4: 6691–6718.

United States Environmental Protection Agency 2015. *EPI Suite™ — Estimation Program Interface* v4.11. Available at https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface.

Winterhalter R., Herrmann F., Kanawati B., Nguyen T.L., Peeters J., Vereecken L. & Moortgat G.K. 2009. The gas-phase ozonolysis of beta-caryophyllene (C(15) H(24)). Part I: an experimental study. *Phys. Chem. Chem. Phys* 11: 4152–4172.